2. In recombination of triplet radical pairs in glycerin, the effect of an internal heavy atom is observed: on introduction of a Br atom in one of the radicals, recombination is accelerated, and the magnetic effect decreases. The intercombination transitions in contact states of radical pairs due to a spin–orbital interaction are important. The contribution of these transitions increases when heavy atoms are present in the system.

LITERATURE CITED

1. P. P. Levin, V. A. Kuz'min, and I. V. Khudyakov, Dokl. Akad. Nauk SSSR, 288, 661 (1986).
2. V. A. Kuz'min, P. P. Levin, and I. V. Khudyakov, Izv. Akad. Nauk SSSR, Ser. Khim., 479 (1986).
3. V. A. Kuz'min, P. P. Levin, and I. V. Khudyakov, Izv. Akad. Nauk SSSR, Ser. Khim., 998 (1987).
4. L. A. Margulis, I. V. Khudyakov, and V. A. Kuzmin (V. A. Kuz'min), Chem. Phys. Lett., 124, 483 (1986).
5. H. Hayashi and S. Nagakura, Bull. Chem. Soc. Jpn., 57, 322 (1984).
6. M. B. Zommt, C. Doubleday, and N. J. Turro, J. Am. Chem. Soc., 107, 6726 (1985).
7. P. P. Levin and V. A. Kuz'min, Izv. Akad. Nauk SSSR, Ser. Khim., 298 (1988).
8. P. P. Levin and V. A. Kuz'min, Dokl. Akad. Nauk SSSR, 292, 134 (1987).
9. A. M. Vasserman and A. L. Kovarskii, Spin Labels and Probes in the Physical Chemistry of Polymers [in Russian], Nauka, Moscow (1986).

CHEMILUMINESCENCE ACCOMPANYING THE THERMAL DECOMPOSITION OF DIETHOXY(tert-BUTYL HYDROPEROXIDATO) ALUMINUM

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The process of the oxidation of organoaluminum compounds by oxygen is accompanied by chemiluminescence, which is excited in reactions involving organoaluminum peroxides (OAP's), i.e., intermediate products of the oxidation process [1]. It was established in an investigation of the oxidation of $(C_2H_5O)_2AlC_2H_5$ (I) that the chemiluminescence appears in luminescent reactions of two different types involving the intermediate of this process $(C_2H_5O)_2AlOOC_2H_5$ (II): a free-radical reaction and a molecular reaction [1]. One of the luminescent reactions may be the thermal decomposition of the organoaluminum peroxide [1]. The purpose of the present work was to study the chemiluminescence appearing during the thermolysis of an organoaluminum peroxide. It is not possible to obtain II in a pure form due to its instability, and the study of the chemiluminescence in reactions involving II formed by the oxidation of I in solution is extremely difficult due to the simultaneous occurrence of reactions with the participation of the organoaluminum compound, organoaluminum peroxides, O_2, and a number of secondary and final oxidation products. Therefore, the relatively stable organoaluminum peroxide $(C_2H_5O)_2AlOOC(CH_3)_3$ was employed as a model compound for the investigation of the luminescence accompanying thermolysis.

EXPERIMENTAL

The peroxide $(C_2H_5O)_2AlOOC(CH_3)_3$ was obtained from $(C_2H_5O)_2AlCl$ in ether according to the method in [2]. The concentration of the organoaluminum peroxide after removal of the solvent was 97%. The organoaluminum peroxide was transferred to ampuls, in which it was stored in a vacuum at 77 K.

The octane used in the optical measurements was prepared according to the method in [3]. The synthesis and purification of galvinoxyl was carried out according to the method in [4]. The kinetics of the decomposition of the organoaluminum peroxide were studied according to the variation of both the intensity of the chemiluminescence and the concentration of the organo-

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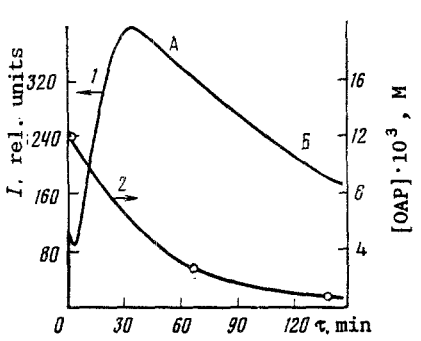

Fig. 1

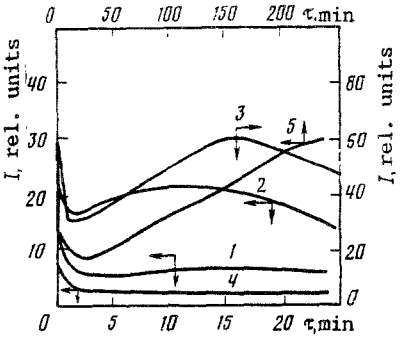

Fig. 2

Fig. 1. Kinetics of the variation of the chemiluminescence intensity (1) and the concentration of the organoaluminum peroxide (OAP) (2) during the thermolysis of $(C_2H_5O)_2AlOOC(CH_3)_3$ (C_0 = $1.2\cdot10^{-2}$ M) in toluene at 353 K.

Fig. 2. Influence of the concentration of the organoaluminum peroxide and the chemistry on the chemiluminescence accompanying the thermolysis of $(C_2H_5O)_2AlOOC(CH_3)_3$ in toluene: $[OAP]_0$ = $4.5\cdot10^{-5}$ (1), $1.6\cdot10^{-4}$ (2), $1.3\cdot10^{-3}$ (3) (1-3, 353 K), and $1.1\cdot10^{-2}$ M (4, 313 K), in a thin layer without a solvent (5, 343 K).

aluminum peroxide, which was determined by iodometric titrations. Before heating, samples of the organoaluminum peroxide were prepared by three methods: for deoxygenation, a weighed portion of the 97% pure organoaluminum peroxide was placed in a quartz ampul, which was sealed in a vacuum (p_{red} = 10^{-4} torr); 2) for minimization of the effect of the internal filter when light is emitted in the thermolysis process, several drops of the 97% pure organoaluminum peroxide were placed between two thin quartz plots, which were tightly clamped to one another and were located on the bottom of a quartz cuvette in an Ar atmosphere; 3) 1 ml of a solution of the organoaluminum peroxide was added to 9 ml of toluene or octane in a quartz cuvette at an assigned temperature. The temperature was monitored with the aid of a thermocouple.

The photoluminescence spectra, as well as the excitation spectra, of solutions in quartz ampuls having a diameter of 0.5 cm were recorded at 77 K on an Hitachi MPF-4 spectrofluorometer.

RESULTS AND DISCUSSION

An analysis of the dependence of the chemiluminescence on the time indicates that the thermolysis of the organoaluminum peroxide is accompanied by more complicated processes than was indicated by the "dark" investigations [2, 5]. Two regions may be singled out. The first includes the abrupt ascent of the intensity of the chemiluminescence and its descent over the course of several minutes (they comprise no more than 15% of the total light sum of the chemiluminescence) and is attributed to reactions of the undetected impurities. Then (in the second region) the chemiluminescence begins to increase and passes through a maximum, after which decay of the luminescence is observed for a long time (Fig. 1). The kinetics of the chemiluminescence has the same character in the case of solutions with concentrations of the organoaluminum peroxide up to 97%. When the concentration of the organoaluminum peroxide is decreased from 10^{-2} to $5\cdot10^{-5}$ M, smoothing of the maximum of the chemiluminescence occurs (Fig. 2). A similar law is also observed when the thermolysis temperature is lowered (Fig. 1, curve 1, and Fig. 2, curve 4). The presence of the maximum is an indication of the participation of an intermediate. The luminous characteristics of the chemiluminescence process accompanying the thermolysis of the organoaluminum peroxide and diphenylethane hydroperoxide [6] are very similar. In [7] it was reported that the decomposition of organoaluminum peroxides takes place according to a homolytic mechanism with the simultaneous cleavage of O—O and Al—O bonds, while preference was given to a heterolytic decomposition path in [2, 5]. The addition of an inhibitor of free-radical reactions, viz., galvinoxyl, into a solution of the thermolyzed organoaluminum peroxide does not cause a decrease in the intensity of the chemiluminescence (Fig. 3, curve 3), but such a decrease occurs in the case of the oxidation of the organoaluminum compound (Fig. 3, curve 4). On the other hand, a bright flash of luminescence lasting about 1.5 min is observed, but is not associated with the reaction of the organoaluminum peroxide with galvinoxyl, since the intensity of the luminescence appearing when the organo-

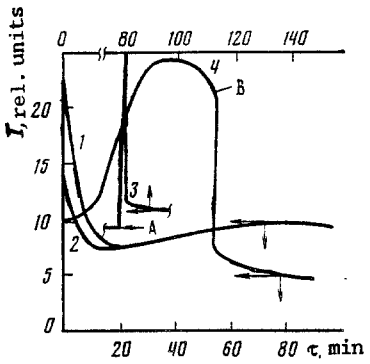

Fig. 3

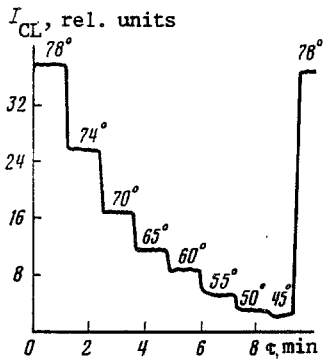

Fig. 4

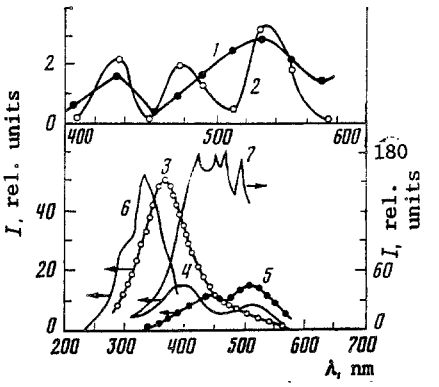

Fig. 5

Fig. 3. Kinetics of the variation of the intensity of the chemiluminescence accompanying the thermolysis of $(C_2H_5O)_2AlOOC(CH_3)_3$ in toluene at 343 K ($[OAP]_0 = 9\cdot10^{-3}$ M): 1) Without galvinoxyl (GL), 2) in the presence of the inhibitor (galvinoxyl was added before the beginning of the thermolysis of the organoaluminum peroxide, $[GL] = 2.5\cdot10^{-5}$ M), 3) galvinoxyl was added at point A ($[GL] = 2.5\cdot10^{-5}$ M), 4) influence of galvinoxyl (point B) on the intensity of the chemiluminescence accompanying the oxidation of $(C_2H_5O)_2AlC_2H_5$ by oxygen.

Fig. 4. Dependence of the chemiluminescence intensity on the temperature in the section of the long descent (A-B) of the luminescence (Fig. 1, curve 1) accompanying the thermolysis of $(C_2H_5O)_2AlOOC(CH_3)_3$ in toluene ($[OAP]_0 = 10^{-2}$ M).

Fig. 5. Chemiluminescence (1, 2), photoluminescence (3-5), and photoluminescence excitation (6, 7) spectra of a solution of $(C_2H_5O)_2AlOOC(CH_3)_3$ in toluene: 1) Without a solvent (353 K), 2) $[OAP]_0 = 9\cdot10^{-3}$ M, 353 K, 3) before heating (λ_{exc} = 315 nm, 77 K, $[OAP]_0 = 10^{-1}$ M), 4) after heating for 2.5 h at 353 K (λ_{exc} = 315 nm, 77 K $[OAP]_0 = 10^{-1}$ M), 5) after prolonged (>20 h) thermolysis at 353 K (λ_{exc} = 315 nm, 77 K, $[OAP]_0 = 10^{-1}$ M), 6) before heating ($\lambda_{p\ell}$ = 395 nm, 77 K), 7) after prolonged (>20 h) thermolysis at 353 K ($\lambda_{p\ell}$ = 495 nm, 77 K).

aluminum peroxide is added to toluene (80 K) is not influenced by the presence of galvinoxyl in it (Fig. 3, curves 1 and 2). The flash of chemiluminescence is a consequence of the reactions of galvinoxyl with intermediate products of the thermolysis of the organoaluminum peroxide, from which radicals of the $RO_2^{\cdot}$ type may be excluded in view of the absence of chemiluminescence when they are interacted with galvinoxyl [1].

The absence of the descent in the intensity of the chemiluminescence when galvinoxyl is added cannot be attributed to a very fast reaction between it and the heated organoaluminum peroxide. It was shown spectrophotometrically that the inhibitor is consumed over the course of ~1.5 min, which is comparable to the time of the chemiluminescence flash. Thus, the generation of luminescence upon the thermolysis of the organoaluminum peroxide probably takes place without the participation of free radicals.

The kinetics of the decomposition of the organoaluminum peroxide in toluene at 40-80°C which were measured by means of iodometric titrations, are exponential (Fig. 1, curve 2). The rate constants k, the activation energy E_a, and the pre-exponential factor A of the decomposition reaction of the organoaluminum peroxide have the following values: $k = 1.2\cdot10^{-3}$ (60°C), $2.3\cdot10^{-3}$ (70°C), and $5.3\cdot10^{-3}$ min^{-1} (80°C); E_a = 7 ± 1 kcal/mole; log A = 6.4 [sec^{-1}]; E_a^1 for section A-B of the slow descent of the chemiluminescence (Fig. 4) is equal to 17 ± 1 kcal/mole; the values of E_a obtained by the two methods are in good agreement. At the same time, the values of the constants determined from the dependence of the intensity of the luminescence on the time in section A-B for different samples of the organoaluminum peroxide differ strongly.

The dependence of the chemiluminescence intensity on the temperature, which can be used to find E_a is measured in a single experiment, allowing us to propose measurements of the chemiluminescence as a quick method for evaluating the activation energy with the use of small quantities of difficultly synthesized organoaluminum peroxides. Thanks to the advantage of the chemiluminescence method, we determined the activation energy E_a^2 of the thermolysis of the 97% pure organoaluminum peroxide (14 ± 1 kcal/mole). Knowing the products of the re-

action [5], we can postulate that the acetaldehyde formed is the emitter of the luminescence accompanying the thermolysis of the organoaluminum peroxide.

The chemiluminescence accompanying the thermolysis of the organoaluminum peroxide appears in the visible region of the spectrum. When the thermolysis of the organoaluminum peroxide was carried out without a solvent (in a "storage" ampul or in a thin layer), the chemiluminescence spectrum contained two broad maxima at 410-460 and 510-550 nm. When the thermolysis of the organoaluminum peroxide was carried out in toluene, the chemiluminescence spectrum contained an additional maximum (460-500 nm) (Fig. 5, curves 1 and 2). The complex form of the chemiluminescence spectrum allows us to postulate the presence of several independent emitters. The close position of the luminescence bands (430 nm) in the chemiluminescence spectrum of the organoaluminum peroxide and the photoluminescence spectrum of acetaldehyde [8] is consistent with the hypothesis that one of the emitters is acetaldehyde.

The photoluminescence spectrum of the original organoaluminum peroxide showed a peak at 380-400 nm (PL_1) (curve 3). In the excitation spectrum of PL_1 for $\lambda_{p\ell}$ = 395 nm there is a band with three maxima at 300-315 (a shoulder), 330, and 340-345 nm (a shoulder) (curve 6). The form of the PL_1 band and the excitation spectrum of PL_1 for the original organoaluminum peroxide without a solvent and in toluene and octane is the same (curves 3 and 6), i.e., the observed chemiluminescence and photoluminescence are not associated with the solvent. These characteristics also remain unchanged after the decomposition of the organoaluminum peroxide (treatment with water). Therefore, the luminescence of the original samples of the organoaluminum peroxide is not directly associated with the organoaluminum peroxide itself. In addition, the photoluminescence spectra of a number of compounds used in the synthesis of the organoaluminum peroxide (ether, tert-butyl hydroperoxide, diethylamine, and diethoxyaluminum chloride) contain maxima in the 350-400-nm region. In addition, some compounds luminesce before heating due to the presence of impurities which are difficult to remove, while others luminesce after heating. Thus, the photoluminescence of the original sample has an impurity character. These impurities do not participate in the chemiluminescence accompanying the thermolysis of the organoaluminum peroxide, as is evinced by the form of the chemiluminescence spectrum recorded during the thermolysis of the peroxide (curves 1 and 2).

After the thermolysis of the organoaluminum peroxide, the form of the photoluminescence and photoluminescence excitation spectra changes significantly. The photoluminescence spectrum displays the formation of a new maximum at 490-520 nm (curves 4 and 5) with simultaneous displacement of the PL_1 maximum toward longer wavelengths. The excitation spectrum of PL_2 (for $\lambda_{p\ell}$ = 495 nm) contains an intense band located at $\lambda > 400$ nm and consisting of a number of narrow, well resolved peaks with λ_{max} = 420, 450, 465, and 485 nm (curve 7). Replacement or elimination of the solvent results only in some redistribution of the intensities of these peaks, while the overall structure of the maximum is maintained. A comparison of the excitation spectra of PL_1 and PL_2 shows that there are two independent emitters. The photoluminescence and photoluminescence excitation spectra of the compounds used in the synthesis of the organoaluminum peroxide and mixtures of these compounds (before and after heating in the absence of the organoaluminum peroxide) do not contain maxima at 400 nm. The PL_2 band is likewise not excited after thermolysis of the organoaluminum peroxide, if it is preliminarily treated with water. Thus, PL_2 is caused by one of the thermolysis products of the organoaluminum peroxide, which has not yet been successfully identified. The emitter of PL_2 may be a complex compound of aluminum formed as a result of the thermolysis of the organoaluminum peroxide. The same compound is apparently the emitter of the chemiluminescence during the thermolysis of the organoaluminum peroxide, since the positions of the long-wavelength maximum in the chemiluminescence spectrum and PL_2 coincide. The study of the chemiluminescence carried out, the results of the spectroscopic measurements, and the literature data [5] allow us to postulate the following scheme for the thermolysis of the organoaluminum peroxide (OAP) with the formation of products mainly in excited states:

$$(1)\ (CH_3)_3COH \longleftarrow (C_2H_5O)_2AlOOC(CH_3)_3 \rightarrow CH_3CHO \quad (3)$$

$$(2)\ (C_2H_5OAl{-}O)_x \longleftarrow \rightarrow (CH_3CHO)^* \rightarrow CH_3CHO + h\nu_{(430\ nm)} \quad (4)$$

$$\rightarrow P_1 \rightarrow P_2^* \rightarrow P_2 + h\nu_{(510\ nm)} \quad (5)$$

$$CH_3CHO \xrightarrow{A-OR} CH_3COOR \quad (6)$$

$$CH_3CHO \xrightarrow{OAP} CH_3COOH + AlOC(CH_3)_3 \quad (7)$$

$$CH_3CHO \xrightarrow{OAP} Al{-}OCOC(CH_3)_3 \quad (8)$$

where P_1 and P_2 are unidentified products.

This scheme more fully reflects the reactions which take place during the thermolysis of the organoaluminum peroxide than does the scheme in [5], since it takes into account products not only in their ground states, but also in their electronically excited states. The occurrence of reaction (4) results in the formation of molecules of acetaldehyde in an excited state, which subsequently undergo a transition to the ground state with the emission of light with $\lambda = 430$ nm. The second chemiluminescent reaction (5) involves the formation of the unstable intermediate P_1, from which the product P_2 forms in an excited state. The transition of P_2 to its ground state is accompanied by the emission of light with $\lambda > 500$ nm. Reaction (5) is responsible for the formation of the maximum on the kinetic curve of the chemiluminescence during the thermolysis of the organoaluminum peroxide. Process (5) may represent reactions involving the conversion of acetaldehyde [6-8].

CONCLUSIONS

The thermolysis of diethoxy(tert-butyl peroxide)aluminum takes place with the formation of products in electronically excited states without the participation of free radicals. One of the emitters of luminescence is acetaldehyde.

LITERATURE CITED

1. G. A. Tolstikov, R. G. Bulgakov, and V. P. Kazakov, Usp. Khim., 11, 1789 (1985).
2. V. A. Dodonov, L. P. Stepovik, and S. M. Sofronova, Zh. Obshch. Khim., 51, 2730 (1981).
3. Modern Methods of Organic Synthesis [in Russian], Izd-vo LGU, Leningrad (1974), p. 144.
4. M. S. Kharasch and B. S. Joshi, J. Org. Chem., 22, 1435 (1957).
5. V. A. Dodonov, L. P. Stepovik, S. M. Sofronova, and D. F. Grishin, Zh. Obshch. Khim., 53, 2527 (1983).
6. V. I. Papisova, V. Ya. Shlyapintokh, and R. F. Vasil'ev, Usp. Khim., 34, 1416 (1965).
7. Yu. N. Anisimov and S. S. Ivanchev, Zh. Obshch. Khim., 16, 2248 (1971).
8. S. McGlynn, T. Azami, and M. Kinoshita, Molecular Spectroscopy of the Triplet State, Prentice-Hall, Englewood Cliffs, New Jersey (1969).

REACTION OF ELECTROCHEMICALLY GENERATED RADICAL ANIONS WITH PHOSPHORYLATED UREAS

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Phosphorylated ureas (PU), which are biologically active compounds, have a number of useful properties [1, 2]. Electron transfer processes occupy a special position in the possible transformations of PU, including those studied here (I)-(VIII), since in [3, 4], they are considered the first stage in oxidation reactions, in the metabolism of organic compounds in environmental objects and in living organisms.

$$(RO)_2P(O)NHC(O)NH_2 \quad (I)-(VIII)$$

R = C_2H_5(I), C_3H_7(II), C_4H_9(III), C_5H_{11}(IV), C_6H_{13}(V), $(CH_3O)_2P(O)NHC(O)NHC_3H_7$(VI), $(C_3H_7O)_2P(O)NHC(O)N(C_2H_5)_2$(VII), $(ClCH_2)_2P(O)NHC(O)NHC(O)NH_2$(VIII).

A mercury cathode and organic electron carriers, radical anions (RA) of oxygen, nitrobenzene (IX), benzophenone (X), and anthracene (XI), were used as electron sources. The reaction of PU with RA of O_2 is of independent interest due to its diffusion in living nature and participation in the vital processes of organisms. The presence of a mobile hydrogen

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